CHAPTER II
LITERATURE REVIEW

Regarding to some previous works, basic information of on-going efforts in MWCNT synthesis and its applications could be summarized as follows,

2.1 Synthesized carbon nanoparticles

Hou et al. also reported that single-wall carbon nanotubes (SWCNTs) and well-aligned thin multi-walled carbon nanotubes (MWCNTs) were successfully synthesized via pyrolysis of a powder mixture of ferrocene and anthracene or 9, 10-dibromoanthracene. The size of the MWCNTs can be tuned just by changing the ratio of ferrocene/anthracene in the mixture. A lower ratio resulted in low-diameter MWCNTs containing up to only five graphene layers. However, a high ratio has led to thick MWCNTs with more than 25 layers and the pyrolysis of pure ferrocene in a hydrogen flow that mainly gives rise to metal nanoparticles. When powder mixtures of ferrocene and 9, 10-dibromoanthracene were pyrolyzed, both SWCNTs and spherical carbon-coated iron nanoparticles were obtained [3].

Satishkumar et al. made use of gas-phase pyrolysis of acetylene along with a metallocene or with a binary mixture of metallocenes in a flowing stream of Ar or Ar + H_2 at 1100 °C to synthesize single-walled carbon nanotubes (SWNTs). Pyrolysis of $Fe(CO)_5$-acetylene mixtures in Ar at 1100 °C could give single-walled nanotubes. The diameter of the SWNTs was generally around 1 nm, showing thereby that on pyrolysis under the dilute conditions, the organometallic precursors could give rise to very fine metal particles essential for the formation of SWNTs [4].

Satishkumar et al. prepared aligned nanotube bundles by pyrolysis of ferrocene along with methane, acetylene or butane. Ferrocene–acetylene mixtures were found to be ideal for the production of compact aligned nanotube bundles. The nanotubes bundles were associated with iron nanoparticles of diameters in the range 2 13 nm. These nanoparticles are ferromagnetic, showing low saturation magnetization compared to bulk iron. The ferromagnetism of the transition metal nanoparticles is likely to be responsible for the alignment of the nanotubes [6].

Charinpanitkul et al. showed that co-pyrolysis of ferrocene and naphthalene could be utilized for synthesis of carbon nanoparticles which are carbon nanotubes (CNTs) and carbon nanocapsules (CNCs), which contained Fe particles in their carbon shells, were simultaneously fabricated. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses revealed that morphology and size of the carbon nanostructure strongly depended on the pyrolysis temperature. At a higher temperature, formation of CNCs would become more enhanced. Particle size distribution and yield of the synthesized products were also significantly influenced by the pyrolysis temperature [7].

Bai et al. synthesized carbon nanostructures by a floating catalyst method. Carbon nanotubes (CNTs) and carbon nanofibers CNFs with different diameters and structures can be obtained by controlling the ferrocene (catalyst precursor)/benzene (carbon source) molar ratio. Nominal diameter of CNFs and CNTs increased while ferrocene/benzene molar ratio was decreased. SWNTs could be synthesized when ferrocene/benzene molar ratio was above 15.1% meanwhile MWNTs could be produced when ferrocene/benzene molar ratio was between 4.2% and 8.76% and CNFs could be synthesized when the ratio of ferrocene/benzene was below 4.2% [8].

Sano et al. showed that Fe-containing CNCs and CNTs were separately formed by pyrolysis of ferrocene in a pure H stream through a cylindrical furnace with a temperature profile controlled at 1050 °C in its center. The CNTs and CNCs were, respectively, formed at the 988 °C zone and colder downstream zone of 625 °C. The CNCs were observed to have an iron carbide core. Typical CNC particle sizes were in the 11 30 nm diameter size range with 2 40 graphitic shells [9].

Lu et al. synthesized carbon-encapsulated Fe nanoparticles via a picric acid-detonation-induced pyrolysis of ferrocene. And they found the nanoparticles exhibit well-constructed core–shell structures, with bcc-Fe cores and graphitic shells and the graphitic shells can protect effectively the cores against the attack of HNO_3 solution. The core–shell nanoparticles are preferably formed at low C/Fe atomic ratios, while tubular structures are formed at high C/Fe ratio. Spheroidal Fe nanoparticles have a narrow diameter distribution of 5 20nm. From XRD analysis they could not found iron carbides in these products. The absence of carbides in these samples is possibly associated with the special high temperature environment [10].

Zhang et al. has recently studied of reaction temperature and duration of the growth of aligned carbon nanotube arrays. Layered aligned multi-wall carbon nanotube (MWNT) films have grown directly by pyrolysis of ferrocene in xylene with the help of cobalt powder. The results indicated that the obtained products composed of many separated layers with MWNTs. The reaction temperature significantly influenced the alignment of the MWNTs, and an appropriate reaction temperature range for growth was 800 900°C. Besides temperature, the reaction duration influenced the length of the well-aligned carbon nanotubes [11].

Kobayashi et al. investigated single-walled carbon nanotube (SWNT) growth using a novel Fe_3O_4 nanoparticle catalyst synthesized with a simple organic chemistry process. Discrete nanoparticles with a uniform diameter of ~4 nm could be deposited on Si substrates with a thermal oxide layer by spin-coating with a nanoparticle solution. These nanoparticles were found to have remarkable catalytic activity in the CVD growth of the SWNTs. SWNTs with diameters of around 1 nm were produced from the reduced nanoparticle catalyst. The diameters of the grown SWNTs were closely correlated with those of the catalytic nanoparticles and tended to be slightly smaller than the particle size [12].

Li et al. have discussed on the growth mechanism which involved in two sizes of iron nanoparticles. While the small particle is catalytically active for the nucleation of the nanotube, the large particle produces the carbon atomistic species required for the growth of the nanotubes. From TEM analysis showed that the diameters of the nanotubes are significantly larger than those of the nanotubes grown at a lower temperature. The aligned nanotubes are believed to be the result of a competition growth process along the normal direction of the substrate. The surface diffusion of carbon atoms on the large iron particle leads to the formation of the observed bamboo-like structure [13].

Lee et al. have grown aligned carbon nanotubes by pyrolysis of ferrocene and acetylene in the temperature range 700 1000°C. As the temperature increases, the growth rate increases by 60 times and the relative amount of crystalline graphitic sheets increases significantly. However, the length of aligned CNTs reaches up to 3 mm at 1000°C. The Arrhenius plot yields the activation energy 35±3 kcal/mol, which is close to the diffusion energy of carbon in bulk γ-Fe. It can be suggested that the bulk diffusion of carbons would play an important role in the growth of cylindrical structured carbon nanotubes [14].

2.2 Application of MWCNTs on removal dye pollutants

Qu et al. prepared MWCNTs filled with Fe_2O_3 nanoparticles via hydrothermal reaction of shortened MWCNTs in ferric nitrate solution and subsequent calcinations. The prepared magnetic MWCNTs can be well dispersed in the water and can be easily magnetic separated from the medium after adsorption. The adsorption capacities for MB and NR in the concentration range studied at pH 6 are 42.3 and 77.5 mg/g, respectively. It is a superior absorbent for the removal of NR and MB from wastewater. Compared with other absorbents, the magnetic nanotubes not only have high adsorption efficiency to dyes, but also can be easily manipulated by external magnetic field [15].

Gong et al. reported that the magnetic MWCNTs nanocomposite adsorbent for effective cationic dye removal has been prepared. The adsorption capacity of the adsorbent towards cationic dyes such as MB, NR and BCB was illustrated by experimental adsorption isotherms at room temperature. The results suggested that the adsorption capacity of three cationic dyes on MMWCNT adsorbent increased with temperature Cationic dyes adsorbed increased with pH due to the electrostatic attraction between the negatively charged MMWCNT adsorbent surface and the positively charged cationic dyes. The prepared magnetic multi-wall carbon nanotubes adsorbent with a surface area ($61.74 m^2/g$) displayed the main advantage of separation convenience compared to other adsorbents [16].

Wu investigated the adsorption efficiency of carbon nanotubes for Procion Red MX-5B at various pHs and temperatures. The amount adsorbed increased with the CNTs dosage; however, the adsorption capacity initially increased with the CNTs dosage (<0.25 g/l) and then declined as the CNTs dosage increased further (>0.25 g/l). The linear correlation coefficients and standard deviations of Langmuir and Freundlich isotherms were determined and the results revealed that Langmuir isotherm fitted the experimental results well. Kinetic analyses were conducted using pseudo first and second-order models and the intraparticle diffusion model. The regression results showed that the adsorption kinetics were more accurately represented by a pseudo second-order model. Moreover, Wu's study suggested that the adsorption of Procion Red MX-5B onto CNTs was physisorption [17].

Kuo et al. reported the feasibility of removing direct dyes Direct Yellow 86 (DY86) and Direct Red 224 (DR224) from aqueous solutions using carbon nanotubes (CNTs). Pseudo second-order and intraparticle diffusion were adopted to evaluate experimental data and thereby elucidate the kinetic adsorption process. Additionally, this study used the Langmuir, Freundlich, Dubinin and Radushkevich (D–R) and Temkin isotherms to describe equilibrium adsorption. The adsorption percentage of direct dyes increased as CNTs dosage and temperature increased. The pseudo second-order model best represented adsorption kinetics. Based on the regressions of intraparticle diffusion model, experimental data suggested that the adsorption of direct dyes onto CNTs involved intraparticle diffusion, but that was not the only rate-controlling step. The equilibrium adsorption of DR86 is best fitted in the Freundlich isotherm and that of DR224 was best fitted in the D– R isotherm. The capacity of CNTs to adsorb DY86 and DR224 was 56.2 and 61.3 mg/g, respectively [18].

Luo and Zhang prepared maghemite nanoparticles with a submerged circulation impinging stream reactor (SCISR).The cellulose beads containning Fe_2O_3 nanoparticles exhibited sensitive magnetic response, and their recovery could facilitate by applying a magnetic field. The adsorption and desorption of the organic dyes on MCB-AC were investigated to evaluate the removal of dyes (methyl orange and methylene blue) with different charges from aqueous solution. Their adsorption kinetics experiments were carried out and the data were well fitted by a pseudo-second-order equation. The results revealed that the MCB-AC sorbent could efficiently adsorb the organic dyes from wastewater, and the used sorbents could be recovered completely [19].

Zhu et al. prepared chitosan wrapping magnetic nanosized γ-Fe_2O_3 and multi-walled carbon nanotubes (m-CS/γ-Fe_2O_3/MWCNTs) under relative mild conditions. Adsorption of methyl orange (MO) onto m-CS/γ-Fe_2O_3/MWCNTs was investigated with respect to pH, initial MO concentration and temperature. Results of characterizations indicated that magnetic nanosized c-Fe2O3 and MWCNTs have been wrapped by crosslinked chitosan. Kinetics data and adsorption isotherm were better fitted by pseudo-second-order kinetic model and by Langmuir isotherm, respectively. After adsorption, m-CS/γ-Fe_2O_3/MWCNTs could be effectively and fleetly separated by applying a magnetic field [20].

Based on literature reviews, it might be implied that carbon nanoparticles, which was synthesized by thermal co-pyrolysis with the mixture of ferrocene and any carbon sources, are a promising novel solid adsorbent for removal dye pollutants. Furthermore, it could be separated from the aqueous solution by magnetic system due to its magnetic properties.